

# Model-Free Kinetics: Curing Behavior of Phenol Formaldehyde Resins by Differential Scanning Calorimetry

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Received 20 November 2001; accepted 15 April 2002

**ABSTRACT:** Isoconversional analysis was used to treat nonisothermal DSC data and yield the dependence of activation energy on conversion during the curing process of PF resins. The shape of the dependence revealed that the curing process of PF resins displayed a change in the reaction mechanism from a kinetic to a diffusion regime. In the kinetic regime a comparative DSC experimental analysis between monomer mixtures and PF resins showed that the addition reactions between phenol and formaldehyde had been mostly completed during the synthesis of PF resins and that the main kinetic reactions contained parallel condensations in the curing process. For the diffusion regime a modified equation for the diffusion rate constant,  $k_d = D_0 \exp(-E_d/RT + K_1\alpha + K_2\alpha^2)$ , is proposed. This equation is in

good agreement with the experimental dependence of  $E_\alpha$  on  $\alpha$  in the diffusion regime, which shows the effect of both temperature and conversion on diffusion. A prediction of the conversion advancement with the reaction time under isothermal condition for PF resin has been made. This prediction can be useful in practical applications for evaluating isothermal behavior of thermosetting systems from nonisothermal experimental data. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 433–440, 2003

**Key words:** model-free kinetics; phenol formaldehyde resin; curing of polymer; activation energy; differential scanning calorimetry

## INTRODUCTION

Phenol formaldehyde (PF) resin resins are the polycondensation materials of reaction of phenol with formaldehyde, which have been used extensively because of their high temperature resistance, high char yield, and moderate flame resistance in many areas, especially in coating applications, adhesives, carbonless copy paper, molding compounds, abrasives, laminates, air and oil filters, and in other composites.<sup>1,2</sup> PF resin is one of the few polymers whose production and development work has been steadily increasing because of active research over the past decades. One of the most important research fields is probably the investigation of curing behavior (mechanism and kinetics) because PF, as one of the thermosetting resins, has a very complicated curing process, which includes many individual reactions that occur simultaneously.<sup>2,3</sup> The current investigation sought to understand the reaction characteristics of PF resins that could be suc-

cessfully applied to selecting the appropriate conditions of the curing process, such as the curing temperature and time.

Differential scanning calorimetry (DSC), a thermal analysis technique widely used to measure the temperatures and heat flows associated with material reaction, is a powerful tool for characterizing the curing process of thermosetting systems.<sup>4–9</sup> Kinetic analysis of DSC data helps to evaluate the curing characteristics and take into account the steps of the curing process, which has been established by other methods, such as FTIR and NMR. A useful technique for DSC analysis is model-free kinetics, described by Vyazovkin,<sup>10–12</sup> which is based on the realization that the function of degree of conversion,  $f(\alpha)$ , and the activation energy,  $E_\alpha$ , depend on the degree of reaction conversion,  $\alpha$ , but that they are always the same at a particular degree of conversion, independent of the heating rate used. The basis used for this technique is the activation energy curve as a function of the degree of conversion, which is evaluated using the isoconversional method from three or more dynamic measurements at different heating rates.<sup>13–17</sup> This new formulation requires no knowledge of the reaction model. For the cure of thermosetting systems, the general method taken is to treat kinetic analysis as phenome-

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Contract grant sponsors: NSERC, FCAR, and Laval University.

nological in nature, which ignores the complexity of cure in kinetic calculations. The basic reaction rate equation is described as

$$d\alpha/dt = kf(\alpha) \quad (1)$$

where  $\alpha$  is the degree of conversion,  $k$  is the rate constant,  $f(\alpha)$  is the function of the degree of conversion, and  $t$  is the reaction time. In general,  $k$  is dependent on temperature through an Arrhenius-type equation. Reaction rate eq. (1) can thus be written as:

$$d\alpha/dt = f(\alpha)A \exp(-E/RT) \quad (2)$$

where  $E$  is the activation energy,  $A$  is the preexponential factor. It is assumed that function  $f(\alpha)$  and parameters  $A$  and  $E$  in the above equation are constant at a particular degree of conversion. Therefore, we can obtain a differential equation from eq. (2):

$$d \ln(d\alpha/dt)_\alpha / dT^{-1} = -E_\alpha/R \quad (3)$$

where  $E_\alpha$  is the activation energy at a given degree of conversion. Compared with the ASTM E698 method,<sup>18</sup> which follows only one point of conversion and applies the derived activation energy at the DSC transition maximum to the overall reaction process, the model-free method follows every point of conversion, obtaining the activation energy at each point. Therefore, it can reveal the dependence of  $E_\alpha$  on  $\alpha$  and the complexity of the curing process.

This study's purpose was to apply the isoconversional analysis to the multiple heating rate DSC data during the curing process of phenol formaldehyde resins, deriving the variation of the activation energy as a function of the degree of conversion. The curing mechanism and kinetics will be taken into account according to the basic relationship between the activation energy and the degree of conversion. A prediction of the curing process will be made at different conditions (nonisothermal and isothermal cure).

## EXPERIMENTAL

Two liquid PF resins for DSC analysis were synthesized in our laboratory according to a modified method.<sup>19</sup> Liquid phenol (90%) and paraformaldehyde were used as ingredients. Resin A is a low-viscosity phenol formaldehyde resin with formaldehyde/phenol and  $\text{NaOH}/\text{phenol}$  molar ratios of 2.2 and 0.29, respectively. Resin B is a highly condensed and partly crosslinked phenol formaldehyde resin with formaldehyde/phenol and  $\text{NaOH}/\text{phenol}$  molar ratios of 2.5 and 0.38, respectively. For the synthesis of resin A, the reactor vessel was charged with phenol, paraformaldehyde, and water. Then the first sodium hydroxide

was slowly added over a 10-min period, and the temperature was allowed to rise to more than 100°C for 2–3 min, then cooled to 65°C and held at 65°C to a Gardner–Holdt viscosity (25°C) of AB (50–65 cps). After that the resin was cooled to 30°C, the second sodium hydroxide and ammonium hydroxide was added into the resin. For the synthesis of resin B, there are two different points during the synthetic process. First, the reaction was held at a temperature of 95°C to a Gardner–Holdt viscosity of AB, then held at 80°C to viscosity of KL (275–300 cps). The solid content of the resins was determined by a pan solid technique.<sup>20</sup> The solid contents of resins A and B were about 51% and 41%, respectively.

A Mettler DSC 20 with a Mettler TA400 thermal analysis system with STAR<sup>c</sup> software was used in all experiments. Because the adhesives are water based, high-pressure steel crucibles (ME-51140404) that can withstand vapor pressure up to 10 MPa were used. Dynamic scans were made with heating rates of 2°C, 5°C, 10°C, and 20°C/min, respectively, and the scanning temperature ranged from 30°C to 250°C. An isothermal scanning was also done at 120°C and at various times.

The activation energy,  $E_\alpha$ , and preexponential factor  $A$  can be evaluated by the following expression.<sup>13</sup>

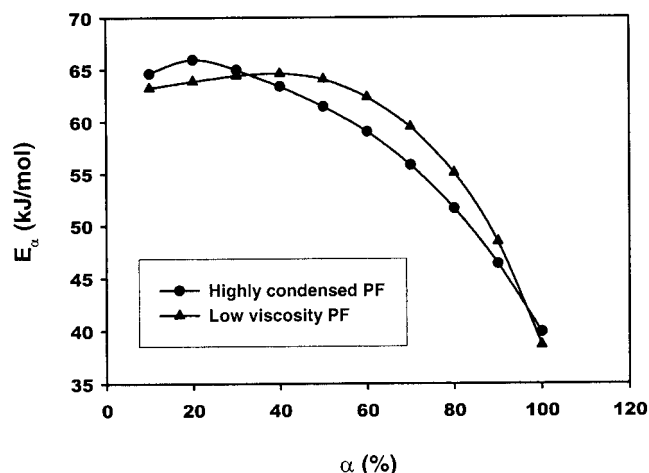
$$\ln \Phi/T_i^2 = -E_\alpha/RT_i + \ln RA/E_\alpha \quad (4)$$

where  $\Phi$  is the heating rate and  $T_i$  is the temperature to reach a given degree of conversion. A plot of  $\ln \Phi/T_i^2$  versus  $1/T_i$  is a straight line from which the activation energy,  $E_\alpha$ , and preexponential factor  $A$  can be obtained from the slope and the intercept, respectively.

## RESULTS AND DISCUSSION

### Dependence of activation energy on degree of conversion

The dependence of activation energy on the degree of conversion for phenolic resin cure calculated by isoconversional method is depicted in Figure 1. The curves indicate that the curing process is accomplished in two stages. The curves<sup>10</sup> that first increased indicate a kinetic process involving parallel reactions or reactions occurring simultaneously. Then they decreased with a convex shape, and this suggests a change in mechanism from kinetic to diffusion stage. In fact, during the cure of thermosetting resins, the reaction systems undergo gelation (from liquid to rubber), vitrification (from rubber to glass) transitions, and crosslinking to reduce molecular mobility and result in a change from a kinetic to a diffusion regime. The plot in Figure 1 shows that the change occurs at a lower degree of conversion for the highly condensed



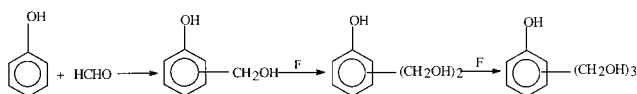
**Figure 1** The dependence of activation energy on the degree of conversion for PF resins.

phenolic resin ( $\alpha = 20\%$ ) than for the low-viscosity one ( $\alpha = 40\%$ ). This is reasonable because the former has reached a higher degree of conversion and viscosity during synthesis of the resin; then the higher viscosity of the reaction system can lead to diffusion regime earlier during the subsequent curing process.

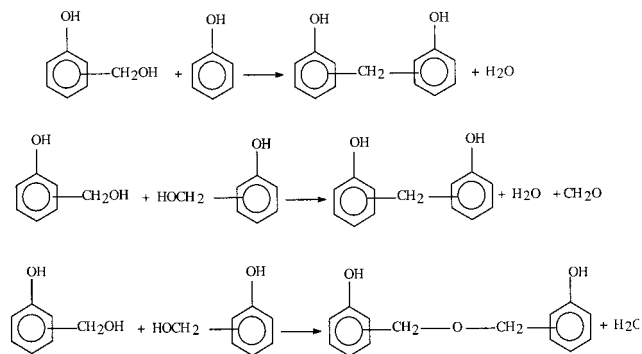
### Kinetics and mechanism in the kinetic regime

It is known<sup>2,3,21</sup> that the main reactions between phenol and formaldehyde in the alkaline pH range are based on two types of reactions: addition of hydroxymethyl groups to the ortho- and para-free positions of phenol, as shown in Scheme 1. Condensation reactions between one hydroxymethyl group and one free position in phenol give rise to a methylene bridge or two hydroxymethyl groups form a methylene ether bond or a methylene bridge (Scheme 2). However, the condensation of two hydroxymethyl groups to form a methylene ether bond is a reaction possible in an acid condition but rare in the presence of alkaline catalysts.<sup>22,23</sup>

DSC analysis indicated that the curing process of phenolic resin was mainly made up of condensation reactions, and the addition reactions were mostly completed during the synthesis of the phenolic resin. The moderately increasing curve in Figure 2 indicates a kinetic process involving parallel reactions, which may be expressed as addition and condensation reactions mentioned above. However, the addition section is very little, and the main reactions are condensations.



**Scheme 1** Additional reactions of phenol formaldehyde resin.

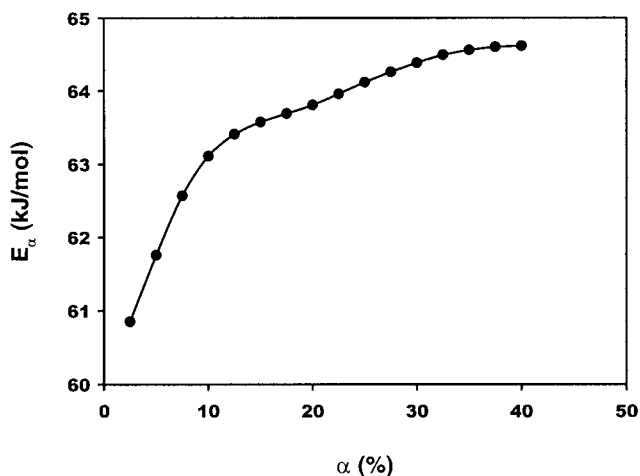


**Scheme 2** Condensation reactions of phenol formaldehyde resin.

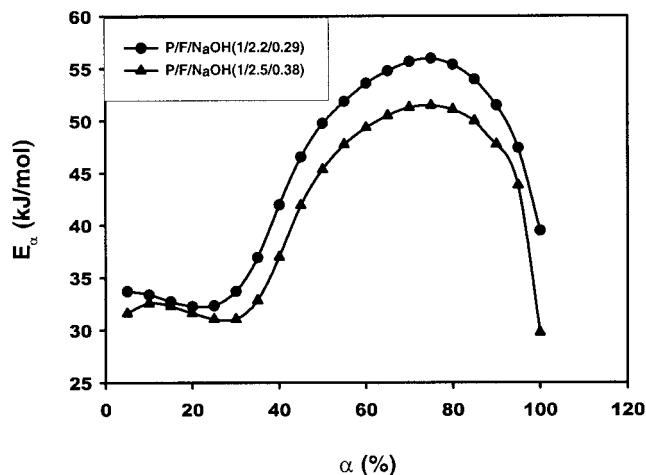
Such a result, the same as from IR analysis,<sup>23</sup> was experimentally confirmed by the following comparative DSC study on reaction behavior of the PF resin and the monomer mixtures of phenol, formaldehyde, and sodium hydroxide. The monomer mixtures were subjected to DSC scans to obtain the dependence of activation energy on conversion (Fig. 3).

Figure 3 indicates that the reaction process of the mixtures, which started with small molecules, contains three main steps. The activation energy that decreased as a concave shape before 30% degree of conversion is characteristic of an intermediate reversible process,<sup>10</sup> which contains addition reactions between phenol and formaldehyde, expressed in Scheme 3.<sup>2</sup> The addition kinetics of the base-catalyzed phenol-formaldehyde reaction was observed as a second-order reaction with the exception of the ammonia-catalyzed reaction, which surprisingly corresponds to a first-order reaction.<sup>2</sup>

The second step of the reaction process of the mixtures is an increase in the degree of conversion from 30% to 70%, in which the curves increase and reach a fairly constant value because of a kinetic process in-

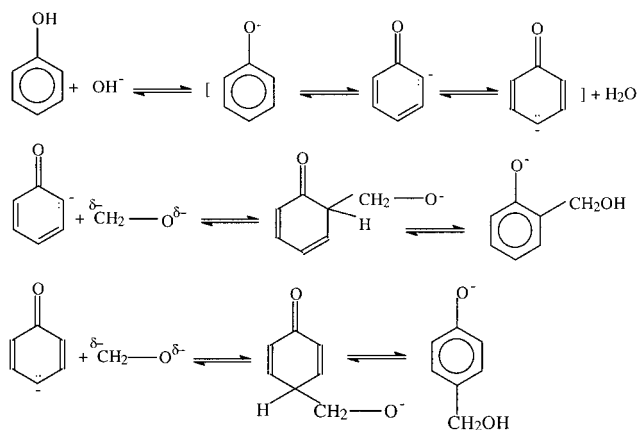


**Figure 2** The dependence of activation energy on conversion for low-viscosity PF resin.

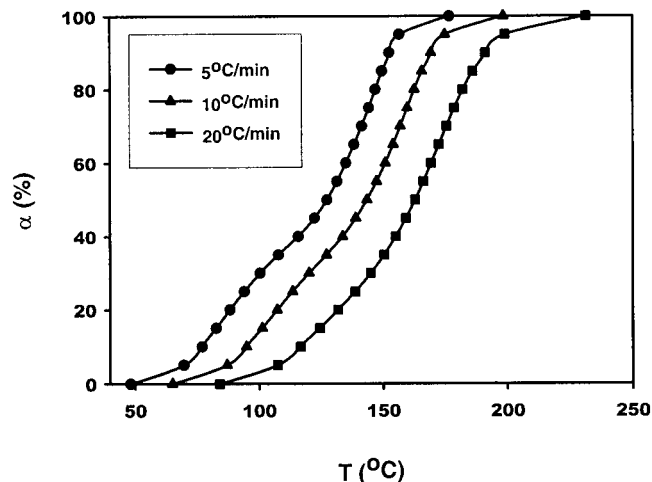


**Figure 3** The dependence of activation energy on the degree of conversion for the mixtures of monomers of phenol, formaldehyde, and sodium hydroxide.

volving parallel reactions. This case is similar to the result in the early stage of the curing process of PF resins, but the increased value of activation energy (more than 20 kJ/mol) was much more than that in PF resin (about 4 kJ/mol). In such a case, for mixtures of monomers, the reactions include two kinds of reactions occurring simultaneously, which are addition and condensation reactions. The addition fraction starts to decrease and the condensation one simultaneously to increase with the increasing activation energy. Therefore, it is reasonable to consider that the condensations are dominant near the end of this step. However, the activation energy in kinetic regime for PF resins increases a little, indicating that the addition section has been almost completed. This is similar to the latter section of the second step during the reaction process of the mixtures. After a 70%–80% degree of conversion, the curves take on a downward convex shape, which is a result of the process with a change from kinetic to diffusion regime.

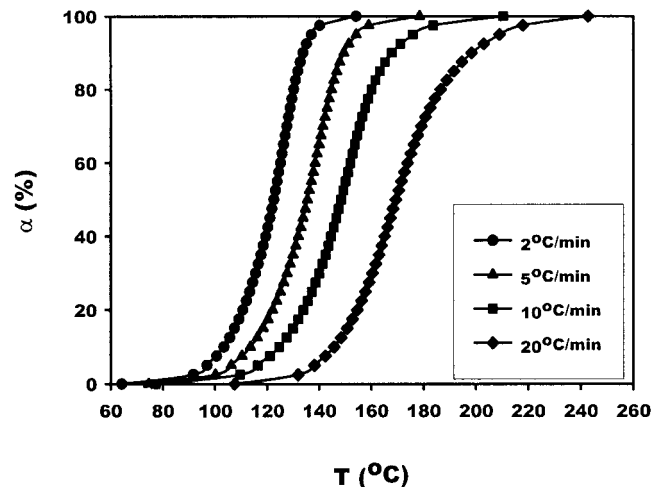


**Scheme 3** An intermediate reversible process of additional reactions for PF resin.



**Figure 4** The conversion advancement with temperature for monomer mixtures (P/F/NaOH = 1:2.2:0.29).

Compared with the degree of conversion changes with the reaction temperature for the monomer mixture and the phenolic resin (shown in Figs. 4 and 5), it is clear that a curvature change of the degree of conversion curves for the monomer mixture can be observed at 30%–40% degree of conversion. This change probably results from a change in the reaction mechanism (from additions to two parallel reactions). In a comparison of the DSC scanning curves of the PF resin and the mixture of monomers, the latter shows two peaks with a dip between them (Figure 6). It is a plausible assumption that there are two dominant reactions involved and that the curve is composed of two individual ones with overlapping final and initial parts during reactions of the mixtures of the monomers.<sup>24</sup> However, the first peak is absent in the DSC curve of PF resin, and this suggests that only one main kind of reaction occurs in the curing process of PF



**Figure 5** The conversion advancement with temperature for low-viscosity PF resin.

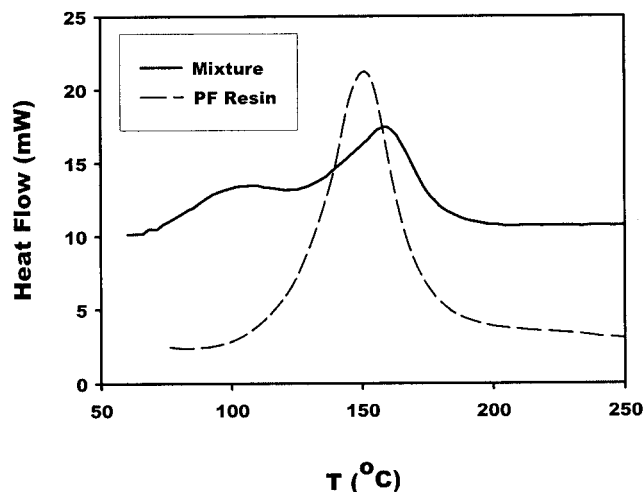


Figure 6 DSC scanning curves of the mixture of monomers and low-viscosity PF resin.

resins. The peak in the curve of PF resin is almost at the same temperature range as the second peak in the curve of the monomer mixture.

The comparative study above shows that the addition reactions are almost completed, and condensations are the main reactions during the curing process of phenolic resins, even though addition reactions can occur simultaneously to the formation of high-molecular-weight species by condensation reactions<sup>21</sup> because of the possibility of formaldehyde being released from the curing systems. The change in activation energy for PF resin is very small, with a change in 4 kJ/mol (from 60.9 kJ/mol to 64.6 kJ/mol) during the kinetic process of condensation reactions. Such a small change indicates that the individual condensation reactions are similar to each other in the reaction mechanism. So the kinetic process of condensation cure of phenolic resin can be reasonably depicted as a one-step reaction, which is a first-order reaction.<sup>23,25</sup>

### Diffusion kinetics and mechanism

For the curing process of the thermosetting systems, the change from kinetic to diffusion regime is significant because of gelation, vitrification, and intermolecular crosslinking. Considering the diffusion process, the time scale for the overall reaction can be modeled as the sum of the time for the diffusion of the reactants plus the time for the chemical reaction<sup>26,27</sup>:

$$\frac{1}{k_a(\alpha, T)} = \frac{1}{k(T)} + \frac{1}{k_D(\alpha, T)} \quad (5)$$

where  $k_a$  is the overall rate constant,  $k$  is the Arrhenius rate constant for chemical reactions, and  $k_D$  is the diffusion rate constant ( $1/k_D = \tau$ , the average polymer segmental relaxation time).

The dependence of  $k_D$  on temperature can be expressed by the Arrhenius form<sup>28</sup>:

$$k_D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (6)$$

This equation is convenient for analyzing the effect of temperature on both diffusion and viscosity. The activation energy of the curing process concerned with diffusion can be calculated by substituting eq. (6) into eq. (5) and making a differentiation to obtain the following equation:

$$E_\alpha = -Rd \ln(k_a)/dT^{-1} = (kE_D + k_D E)/(k + k_D) \quad (7)$$

However, there are some explicit defects in this method for calculating  $E_\alpha$  in the diffusion regime because the effect of temperature on diffusion is not the only factor. The constant  $k_D$  is directly concerned with the mobility of the molecules and their segments in the reaction systems, which is affected by the change of physical properties and viscosity related to the degree of conversion. For thermosetting systems,<sup>29,30</sup> there is an immense change in viscosity because of gelation, vitrification, and intermolecular crosslinking during the curing process. Concerning the molecular diffusion in the curing process, a diffusion coefficient has been obtained as<sup>31</sup>

$$D = D_0 \exp\{B[1 - (f_g + \alpha_f(T - T_g))^{-1}]\} \quad (8)$$

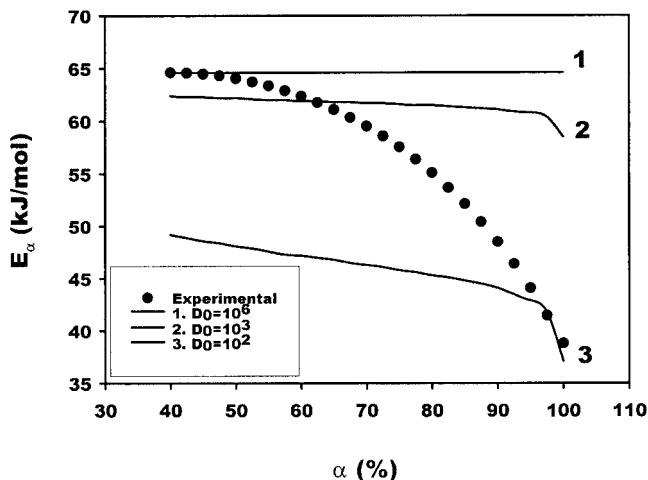
where  $f_g$  is the fractional free volume at  $T_g$  and  $\alpha_f$  is the thermal expansion coefficient of the free volume. This equation requires the experimental determination of the dependence of  $T_g$  on  $\alpha$ , and then a relationship between  $k_D$  and  $D$  to calculate  $k_D$ .

Another semiempirical relationship based on free-volume considerations has been applied to the diffusion effect.<sup>32-34</sup> It relates the diffusion-controlled rate constant,  $k_D$ , to the chemical rate constant,  $k$ , as follow:

$$k_D = k \exp[-C(\alpha - \alpha_c)] \quad (9)$$

where  $C$  is a fitted parameter and  $\alpha_c$  is the critical conversion. This semiempirical equation indicates that the degree of conversion influences the diffusion reaction in the curing system. It may be noted that the critical conversion,  $\alpha_c$ , corresponds to an abrupt onset of diffusion control, whereas the onset is gradual in real reactions. Furthermore, the diffusion rate constant resulting from the reduced mobility of reaction species seems not to be closely related to the chemical rate constant.

A simplified method is based on eq. (6), which is an explicit function of  $k_D$  as  $T$  modified in consideration of both the effects of temperature and conversion on



**Figure 7** The dependence of activation energy on conversion for low-viscosity PF resin ( $K = 0$ ).

activation energy in the diffusion regime. An equation<sup>35</sup> has been used to describe the change in viscosity with conversion and temperature:

$$\mu(T, \alpha) = \mu_0 \exp(E_\mu/RT + K\alpha) \quad (10)$$

where  $\mu$  is the viscosity of the reaction systems,  $\mu_0$  is the preexponential factor,  $E_\mu$  is the activation energy of viscous flow, and  $K$  is a constant accounting for the effect of conversion of reaction on the change in the viscosity of reaction systems. Considering that  $1/k_D = \tau$ , which is the average polymer segmental relaxation time, can be proportional to the viscosity, an analogous equation to eq. (10) can be introduced<sup>12</sup>:

$$k_D(T, \alpha) = D_0 \exp(-E_D/RT + K\alpha) \quad (11)$$

This equation establishes explicit dependence of  $k_D$  on temperature and conversion. Substituting eq. (11) into eq. (5) with the following differentiation gives the same expression for  $E_\alpha$  as eq. (7); however,  $k_D$  is expressed by eq. (11).

To calculate the dependence of  $E_\alpha$  on  $\alpha$ , the values of  $E$  and  $E_D$  were taken from the experimental measurement. Kinetic activation energy,  $E$ , and preexponential factor,  $A$ , have been taken to be 64.6 kJ/mol and  $4.6 \times 10^7$ , respectively.  $E_\alpha$  at  $\alpha \rightarrow 1$  gives a limited estimate for  $E_D$  of 38.8 kJ/mol. In general,  $E_D$  is considered not to be greater than 20 kJ/mol,<sup>28</sup> a value used as an approximation for  $E_D$ . Figure 7 shows the dependence of  $E_\alpha$  on  $\alpha$  without considering the effect of conversion on diffusion. Curves 1 and 2 start with  $E_\alpha$  approaching the experimental data, but they display little change in the influence of diffusion on  $E_\alpha$  at a higher conversion. Curve 3 starts with a much lower  $E_\alpha$  than the experimental data and then displays too early influence of diffusion on  $E_\alpha$ . Figure 8 shows the dependence of  $E_\alpha$  on  $\alpha$  with considering the effect of

both temperature and conversion on diffusion. The value of the constant  $K$  displays the effect of the degree of conversion on diffusion. A regression analysis is used to evaluate the value of  $K$ . Therefore, we utilize a function of the degree of conversion,  $ft(\alpha)$ , to replace  $K\alpha$ . Then the  $k_D$  can be modified as

$$k_D(T, \alpha) = D_0 \exp(-E_D/RT + ft(\alpha)) \quad (12)$$

Then the function of  $ft(\alpha)$  can be obtained from eqs. (7) and (12) as the following equation:

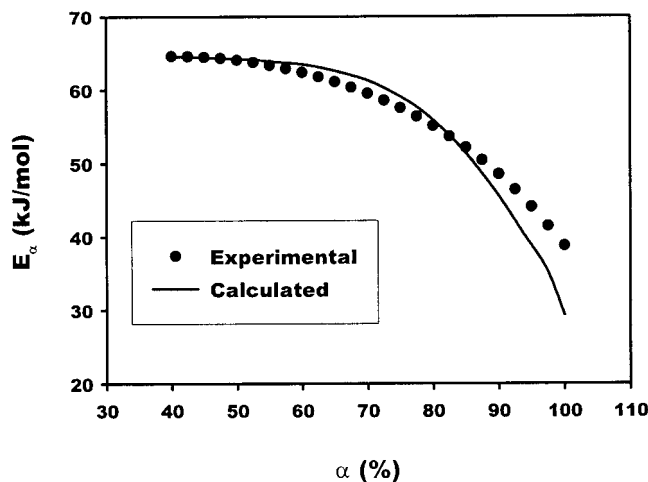
$$ft(\alpha) = \frac{E_D}{RT} + \ln \frac{k(E_\alpha - E_D)}{D_0(E - E_\alpha)} \quad (13)$$

The function of  $ft(\alpha)$  is calculated at each degree of conversion from eq. (13). A linear regression analysis between  $ft(\alpha)$  and  $\alpha$  yields the function of  $ft(\alpha)$ , that is, the relationship between  $ft(\alpha)$  and  $\alpha$ , which is  $ft(\alpha) = -10.08\alpha$ . The fitted curve obtained at  $K = -10.08$  is in good agreement with the experimental data.

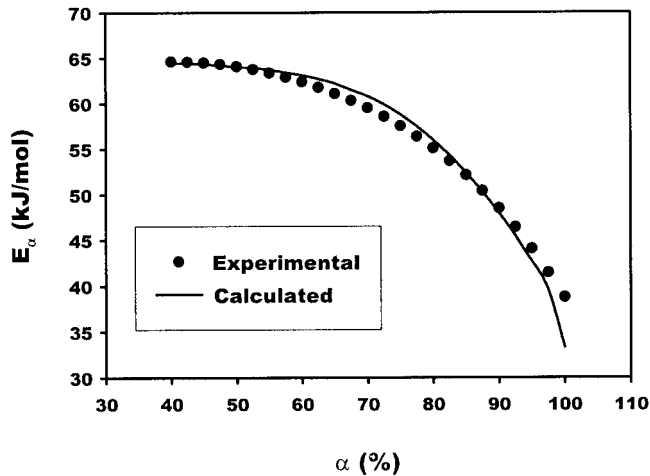
However, there is no linear variation of function  $ft(\alpha)$  with the degree of conversion from the experimental data. This defect can be found in Figure 8. In fact, there is a distribution in molecular size at a certain degree of conversion in the curing system. This distribution leads to a different level of contribution to the diffusion reaction. Considering this different level of contribution at the same degree of conversion, a new equation is proposed by modifying eq. (11) to a quadratic form, which can express more exactly the effect of conversion on diffusion:

$$k_D(T, \alpha) = D_0 \exp(-E_D/RT + K_1\alpha + K_2\alpha^2) \quad (14)$$

A quadratic regression analysis [ $ft(\alpha) = K_1\alpha + K_2\alpha^2$ ] can be used to obtain the constants of  $K_1$  and  $K_2$ , which



**Figure 8** The dependence of activation energy on conversion for low-viscosity PF resin ( $D_0 = 10^6$ ).



**Figure 9** The dependence of activation energy on conversion for low-viscosity PF resin calculated by eq. (11) ( $D_0 = 10^6$ ,  $K_1 = -11.95$ ,  $K_2 = 2.364$ ).

are  $-11.95$  and  $2.364$ , respectively. Figure 9 shows the dependence of  $E_\alpha$  on  $\alpha$ , considering the quadratic effect of conversion on diffusion. It appears that a better fitted curve can be obtained to repeat the experimental dependence of  $E_\alpha$  on  $\alpha$ .

The diffusion model above indicates that both temperature and conversion affect the diffusion rate constant. As mentioned above, the relaxation time for a molecule in a viscous medium is directly proportional to the viscosity. This suggests that diffusion is closely related to viscosity. The temperature and conversion dependence of diffusion mainly results from the effect of temperature and conversion on the viscosity in the system. On the other hand, the effect of conversion on diffusion is a result of the change in molecular weight and molecular structure with the conversion in the system. In general, average molecular weight is a unique function of conversion in a given reaction system. Furthermore, the coefficient of diffusion is predominantly determined by the molecular weight at a given temperature.<sup>36,37</sup> We modified the linear effect of conversion on diffusion into the quadratic effect because of the molecular weight distribution. Different molecular sizes yield different effects on diffusion. In fact, the effect of conversion on diffusion is complicated. Other factors such as molecular structure (linear chain, branched chain, and crosslinked chain), which are also functions of conversion in a reaction system, have effects on diffusion.

#### Prediction of conversion advancement under different conditions

An important aim of this study was to predict the curing behavior for thermosetting resins under different conditions. It is simple to predict a nonisothermal behavior at different heating rates with eq. (4). Substi-

tuting Arrhenius parameters and an arbitrary heating rate at a certain conversion, a corresponding temperature can be obtained from eq. (4). A relationship between conversion and temperature at an arbitrary heating rate can be obtained by calculating corresponding temperatures at different conversions.

It is relatively complicated to predict the isothermal behavior from nonisothermal data. An integrated equation is introduced from eq. (2) at an arbitrary temperature,  $T_{iso}$ :

$$g(\alpha) = tA \exp(-E/RT_{iso}) \quad (15)$$

where  $g(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$  is the reaction model. For a simple reaction including only one step in overall process, such as first-order kinetic reaction, an expression of model  $g(\alpha)$  can be obtained and substituted into eq. (15) to produce a corresponding reaction time at a certain conversion. However, it is not a good idea for a complex reaction that includes several steps to be solved in the same way. If the heating rate,  $dT/dt = \Phi$ , is substituted into eq. (2), then the differential function of conversion on temperature can be obtained:

$$\frac{d\alpha}{dT} = \frac{A}{\Phi} f(\alpha) \exp\left(-\frac{E}{RT}\right) \quad (16)$$

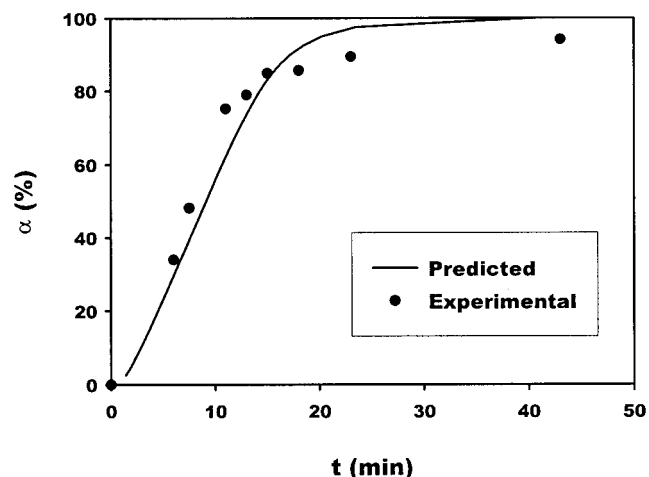
Integrating the above equation to give:

$$g(\alpha) = \frac{A}{\Phi} \int_{T_0}^{T_\alpha} \exp\left(-\frac{E}{RT}\right) dT \quad (17)$$

Compared with eqs. (15) and (17), an equation for the reaction time at a given conversion and an arbitrary isothermal temperature can be obtained:

$$t_\alpha = \left[ \Phi \exp\left(-\frac{E_\alpha}{RT_{iso}}\right) \right]^{-1} \int_{T_0}^{T_\alpha} \exp\left(-\frac{E}{RT}\right) dT \quad (18)$$

Eq. (18) requires an assumption<sup>38</sup> that the reaction model  $g(\alpha)$  and Arrhenius parameters related to a given conversion do not vary with the changing temperature. Figure 10 shows the prediction of the dependence of conversion on the reaction time for PF resin at an isothermal temperature of  $120^\circ\text{C}$  by eq. (18). It shows that the prediction with eq. (18) agrees well with the experimental data. Possible errors may result from the assumptions, which are different from the actual situation. For example, there is a change in activation energy from  $T_0$  to  $T_\alpha$ , which leads to an error in calculating the integration section in eq. (18). Overall, the prediction with eq. (18) has given a good result and can be useful in practical applications.



**Figure 10** The conversion advancement with reaction time at isothermal temperature of 120°C for low-viscosity PF resin.

## CONCLUSION

The experimental dependence of activation energy on the degree of conversion for PF resins from the isoconversional analysis of nonisothermal DSC data can be utilized to interpret the curing mechanism of PF resins. The curing process of PF resins contains a change in reaction mechanism from a kinetic to a diffusion regime because of gelation, vitrification, and crosslinking in the curing systems. In a kinetic regime a comparative DSC experiment shows that the main kinetic reactions contain parallel condensations in the curing process of PF resin preceded by the addition of formaldehyde with phenol at a low degree of conversion. In a diffusion regime the overall process is affected by both kinetic and diffusion reactions. Both temperature and physical properties (related to conversion) of the curing systems simultaneously affect the diffusion of molecules and their segments. A prediction of the conversion advancement with reaction time for PF resin is in good agreement with the experimental data and can be useful in practical applications for evaluating the isothermal curing behavior of thermosetting systems.

The authors thank NSERC, FCAR, and Laval University for funding this research.

## References

- Kopf, P. W. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Interscience: New York, 1988; Vol. 11, p 41.
- Knop, A.; Pilato, L. A. In *Chemistry and Applications of Phenolic Resins*; Springer-Verlag: Berlin, 1985.
- Grenier-Loustalot, M.; Larroque, S.; Grenier, P.; Leca, J.-P.; Bedel, D. *Polymer* 1994, 35, 3046.
- Prime, R. B. *Thermal Characterization of Polymeric Materials*; Turi, E. A. Eds.; Academic Press: San Diego, CA, 1997.
- Wang, X. M.; Riedl, B.; Christiansen, A. W.; Geimer, R. L. *Polymer* 1994, 35, 5685.
- Ivanov, D. A.; Chuvaev, V. F.; Kiselev, M. R. *J Therm Anal* 1992, 38, 1061.
- Apicella, A.; Nicolais, L.; Iannone, M. *J Appl Polym Sci* 1984, 29, 2083.
- Han, C. D.; Lee, G. S. *J. Appl Polym Sci* 1987, 33, 2859.
- Kohl, W. S.; Frei, J.; Trethewey, B. R. *Tappi Journal* 1996, 79(9), 199.
- Vyazovkin, S.; Lesnikovich, A. *Thermochimica Acta* 1990, 165, 273.
- Vyazovkin, S. *Thermochimica Acta* 1992, 194, 221.
- Vyazovkin, S.; Sbirrazzuoli, N. *Macromolecules* 1996, 29, 1867.
- Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
- Ozawa, T. *J Therm Anal* 1970, 2, 301.
- Flynn, J. H.; Wall L. A. *J Polym Sci, Part B* 1966, 4, 323.
- Flynn, J. H. *J Therm Anal* 1983, 27, 95.
- Irabien, A.; Santiago, C.; Araiz, A. *J Therm Anal* 1983, 29, 1131.
- Standard Test Methods for Arrhenius Kinetic Constants for Thermally Unstable Materials ANSI/ASTM E698-79*; ASTM: Philadelphia, 1979.
- Chiu, S.-T. U.S. Pat. 4,433,120 (1984).
- ASTM D4426; Philadelphia, 1993; Vol. 15.06.
- Astarloa-Aierbe, G.; Echeverria, J.; Egiburu, J.; Ormaetxea, M.; Mondragon, I. *Polymer* 1998, 39, 3147.
- Pizzi, A. *Wood Adhesives*, Marcel Dekker: New York, 1983, p 111.
- Carotenuto, G.; Nicolais, L. *J Appl Polym Sci* 1999, 74, 2703.
- Sebenik, A.; Vizovisek, I.; Lapanje, S. *European Polymer J* 1974, 10, 273.
- Kay, R.; Westwood, A. R. *Euro Polym J* 1975, 11, 25.
- Rabinovitch, E. *Trans Faraday Soc* 1937, 33, 1225.
- Wisnarakit, G.; Gillham, J. *J Appl Polym Sci* 1990, 41, 2885.
- Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, London, 1941.
- Peng, W.; Riedl, B. *Polymer* 1994, 35, 1280.
- Kim, Y.; Park, S.; Lee, J. *Polymer J* 1997, 29, 759.
- Huguenin, F.; Klein, M. *Ind Eng Chem, Prod Res Div* 1985, 24, 166.
- Khanna, U.; Chanda, M. *J Appl Polym Sci* 1993, 49, 319.
- Khanna, U.; Chanda, M. *J Appl Polym Sci* 1993, 50, 1635.
- López, J.; López-Bueno, I.; Nogueira, P.; Ramirez, C.; Abad, M. J.; Barral, L.; Cano J. *Polymer* 2001, 42, 1669.
- Lee, W.; Loos, A.; Springer, G. *J Compos Mater* 1982, 16, 510.
- de Gennes, P. G. *J Chem Phys* 1971, 55, 572.
- Rohr, D. F.; Klein, M. T. *Ind Eng Chem Res* 1988, 27, 1361.
- Vyazovkin, S.; Lensnikovich, A. *Thermochim Acta* 1992, 203, 177.